

Wässrige Edelmetallkolloide und ihre Verwendung

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Abstract of **DE 19803891 (A1)**

Aqueous precious metal colloids in the form of a sol with metal particles of 0.5-100 nm containing more than 10 mmol precious metal per litre of sol. Said colloids can be obtained by reduction of a precious metal salt or complex dissolved in water by using an organic reducing agent in the presence of a water-soluble polymer and optionally in the presence of multivalent anions. The aqueous precious metal colloids can be used to produce catalysts with a precious metal support by bringing said colloids into contact with a catalyst support, whereby the precious metal is spontaneously absorbed onto said support.

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The invention relates to of precious metal colloids, D. h. within the nanometer range of high-disperse, ultrafine precious metal particles; they find various application as precursors of supported catalysts.

In J. Colloid interface Sci. 131 (1989), 186 and in J. Colloid interface Sci. 110 (1986), 82 is the preparation of stabilized colloids of noble metals, its application on ion exchange resins and their use as hydrogenation catalysts described. For this solved precious metal salts with NaBH₄ in presence of surface-active Detergenzien become reduced and the precious metal hydraulic brine resultant thereby on the ion exchange resins brought. After the there described method precious metal colloids with a precious metal concentration of at the most 0.5 can be manufactured mmol/l. JP 1/100 545 describes the preparation one likewise 0.5 mmol/l contained palladium hydraulic oil by reduction of solved PdCl₂ with ascorbic acid in presence of Poly N vinylpyrrolidon. In JP 2/179 881 the preparation becomes one up to 10 mmol/l contained Pd-Hydrosols described, whereby PdCl₂ becomes reduced by reduction with NaBH₄ in presence of water-soluble polymers. However '881 hydraulic brine with more than 10 is not producible mmol/l after indications of these JP. Further this hydraulic brine in presence of alkaline-earth chloride becomes prepared. From J. Physical one. Chem. one. 99 (1995), 15934 is the preparation one likewise 10 mmol/l contained Pt-Hydrosols by reduction of H₂PtCl₆ with high concentrations of the combustible methanol in presence of Poly N vinylpyrrolidon known.

These indications show that there is so far no method, in order to manufacture aqueous precious metal colloid solutions with precious metal concentrations of over 10 mmol/l. There one for technical catalysts usually a precious metal content from 0,1 to 20 Gew. - the use so low concentrated metal colloid solutions economic adverse aims at, is %, since large volumes of these colloid solutions used to become to have and only a low space-time yield achieved becomes. Must be fallen back additional for solubility reasons of the used chemicals to organic solvents or their mixtures, other undesirable needs result, since with the subsequent application of the precious metal colloid for instance on activated charcoal-inertial special precautions taken to become to have, in order to exclude self inflammation and general fire risks. The for this required apparatuses raise the price of further the manufacturing process of such supported catalysts.

It is further known (EP 665,265), to manufacture catalytic acting compositions which contain metal particles with an average particle diameter of less than 100 Nm, polymers and particulate support material. Their preparation metal salts in presence of the questioner material become the metal reduced, which draws up immediately on the carrier. Obvious one is feared that a separate prepared Hydrosol is to unstable, in order to let it draw up to late successful on a carrier.

Found that one can manufacture long time stable, also pure aqueous precious metal colloid solutions, in desired manner the precious metal content was contained now of more than 10 mmol/l, if one aqueous solutions with corresponding high maintained ones of precious metal salts in presence or several water-soluble polymere ones with organic reducing agents of a treated. The object according to invention exists thus in the preparation of highly concentrated aqueous precious metal colloids, which the preparation of precious metal supported catalysts used to become favourable to be able and in particular the disadvantages described above avoid.

The invention relates to of aqueous precious metal colloids in form of a sol with metal particles of a size from 0,5 to 100 Nm, those by reduction of precious metal connections by organic reducing agents obtained become and those characterized are through

- a) a precious metal content of more than 10 mmol/l per L sol,
 - b) content at water-soluble polymers from 0,1 to 20 Gew. - %,
 - c) content at organic solvents from 0 to 10 Gew. - %, everything related to the total weight of the sol, and
 - d) the remainder to 100 Gew. - % at waters,
- whereby additional oxidation products of the used reducing agents and excess reducing agents in the sol are present if necessary.

The invention relates to further a method to the preparation of aqueous precious metal colloids with metal particles of a size from 0,5 to 100 Nm, which is characterized by the fact that one to an aqueous solution of a precious metal salt or - complex or several water-soluble polymers adds and then the precious metal cation from them of a reduced, whereby with a metal content of more as 10 mmol/l to 500 mmol/l, several to the metallic state by addition of an organic reducing agent from the group of C1-C4-Alkoholen, C1-C4-Aldehyden, formic acid, ascorbic acid, citric acid, urea or other one to the person skilled in the art known organic reducing agents or a mixture, calculated than elemental metal, an amount of the water-soluble polymer from 0,1 to 20 Gew. - one works %, everything related to the total weight of the aqueous solution.

The invention relates to further a method to the preparation of precious metal supported catalysts, which is characterized thereby that one brings a catalyst support with a precious metal colloid a contained sol to the above type in contact, the noble metal on the carrier draw up lets, so that the finished supported catalyst 0.1 to 20 Gew. - % noble metal, related to

which total weight of the supported catalyst contains, which dries depleted sol remote and the supported catalyst at noble metal.

Noble metals in the sense of the invention are the elements of the so called platinum group and the group Ib of the periodic table (Mendeleev). In detail are mentioned: Palladium, rhodium, ruthenium, platinum, iridium osmium, silver and gold or any mixture of the above metals, preferred palladium, rhodium, platinum and gold, particularly preferred palladium and platinum. The metal particles can become also in the dispersion state with not reducible metal components doped. Such metals are for example Ti, Zn, Zr, Mo, Hf; Re, Ce, Lu, Ni, Cu. Preferred ones are Ni^{2+} or Cu^{2+} . These metals can become as solution of their salts introduced. The amount of these doping metals amounts to 0 to 100 Gew.-%, preferred 0 to 30 Gew.-%, related to the weight of the noble metal and calculated as metal.

Suitable water-soluble polymers are for example polymers and copolymers of monomers with polar groups, like hydroxyl, the revision modification NO, the carboxyl and the sulfonic acid group. They can with monomers without polar group or with a less strong polar group, as the ester group, in such an extent it is copolymerisiert that the water solubility copolymer of the obtained remains. Such monomers are about N-vinyl-pyrrolidon, acrylic acid, methacrylic acid, aspartic acid, styrene-sulfone-acidic, (Meth) Acrylsäure-C1-C4-Alkylester with a hydroxyl, a revision modification NO or a C1-C4 Alkylamincgruppe, the notional monomer vinyl alcohol, N-vinyl-caprolactam, Vinylpyridin, Vinylamin, N-vinyl-imidazol, N-Vinylmethylimidazol; insertable comonomers are for example (Meth) acrylic acid C1-C4-alkylester and vinyl acetate. These (CO) monomers and the methods to their (CO) polymerization are the person skilled in the art known. Preferred polymers are for example Poly N vinylpyrrolidon, polyacrylic acid, polymethacrylic acid, polyvinyl alcohol, Polyasparaginsäure, particularly preferred Poly N vinylpyrrolidon. The polymers have molecular weights (weight averages) of 15.000 to 1.500.000, preferred 30.000 to 1.000.000. They can become single or by them used several as mixture.

Organic solvents, which can be present in the precious metal colloid solutions according to invention, are water-soluble and are for example alcohols, carbonic acids, Ketone and nitriles with up to 4 C-atoms, the methanol, ethanol, propanol, i propanol, Butanol, acetic acid, propionic acid, acetone, methyl ethylketon, acetonitrile. Such solvents can become used, if become used in waters heavy-soluble precious metal complexes. From hygenical working, safety-relevant and environmentalcareful reasons preferred without organic solvents one works. The quantity range for the solvents has therefore the zero as lower bound and amounts to 0 to 10 Gew.-%, related to the total weight of the sol.

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Some in question coming organic solvents can serve however as organic reducing agents.

The invention is further preferred characterized by content at polyvalent anions in the aqueous precious metal colloids. Polyvalent anions of this type are for example: Citrate, phosphate, polyphosphate.

Such polyvalent anions are present in an amount from 0,1 to 10%, related to the total weight of the aqueous precious metal colloids.

The precious metal colloid solutions according to invention are such on aqueous basis. Thus the remainder is to 100 Gew.-% and thus the predominant portion of waters.

Organic reducing agents to the preparation of aqueous precious metal colloids according to invention are the person skilled in the art known and are for example C1-C4-Alkohole, particularly methanol or ethanol, C1-C4-Aldehyde, particularly formaldehyde or acetaldehyde, formic acid, ascorbic acid, citric acid, urea or a mixture several of them. Preferred used becomes: Ascorbic acid, citric acid, methanol, ethanol or a mixture several of them. They become in an amount, related to the stoichiometric need, from 100 to 5.000% used. Preferred one is an amount from 150 to 2.000%, particularly preferred is an amount from 200 to 1.000%. The stoichiometric need is the person skilled in the art known.

To the preparation of the aqueous precious metal colloids according to invention one submits for example an aqueous solution of a precious metal salt or a water-soluble precious metal complex, gives or several water-soluble polymers and or several salts with polyvalent anions to it and to reduced with one of the reducing agents mentioned. If solubility conditions require it, can or the several organic solvents mentioned additional used become. The sequence of being present and admitting can become also arbitrary varied, whereby however the reducing agent becomes preferred used at the conclusion. The noble metal becomes in form of the halides (fluorides, chlorides, bromides, iodides), nitrates, sulfates or in the form of salts of carbonic acids, which can be also substituted by Amino or halogen, used; other possibilities of the use of the noble metals exist in the use of their metal alcoholates, Metallphenolate, Metallacetylacetonate and different the person skilled in the art of common precious metal connections. Such precious metal connections can become also in form of their complexes used; Complex rich of simple double salts, like Na_2PdCl_4 or H_2PtCl_6 up to complex compounds with organic ligands, like Palladiumacetylacetonat.

Carbonic acids, whose precious metal salts, as mentioned above, used are to become to be able, have 1 to 20 C-atoms, linear, branched or cyclic are, further saturated or unsaturated and to have 1 to 3 carboxyl groups. Examples for such carbonic acids are: Formic acid, acetic acid, propionic acid, butyric acid, oxalic acid, adipic acid, citric acid, lactic acid, amino acids, like lysine or aspartic acid.

In the aqueous precious metal colloids according to invention are present the metal particles in a size from 0,5 to 100 Nm, preferred 1 to 30 Nm. The precious metal content in the aqueous precious metal colloids according to invention is always above 10 mg Atom/l, preferred above 50 mg-Atom/l, and achieved values of up to 250 mg-Atom/l, in many cases of up to 500 mg-Atom/l.

Such a aqueous precious metal colloid according to invention can to be become with a catalyst support, as an ion exchange resin, an activated carbon, a M_2O_3 , a SiO_2 and a different one the person skilled in the art common carriers, in contact brought. Here the precious metal colloid draws up spontaneously on the catalyst support. The amount and concentration of the aqueous precious metal colloid in the comparison to the amount of the offered carrier so calculated can become in simple and known manner that the finished supported catalyst 0, 1 to 20 Gew.-% at noble metal, related to which total weight of the supported catalyst contains. Those the carrier with the aqueous precious metal colloid can through entries of the carrier into this aqueous precious metal colloid take place, however also via others the person skilled in the art known procedures, like via Aufsprühen or via addition of the aqueous precious metal colloid to the catalyst support, which becomes moved in a Pelletiertrommel, until the carrier, at its wet condition, is more recognizable

saturated with precious metal colloid. After everyone the described becomes the sol depleted at noble metal remote and the supported catalyst dried.

Examples

Preparation of the metal oil

1. 64 g of an aqueous solution of hexadecimachlorine-platinum-acidic (H_2PtCl_6) of 25 Gew. - % platinum content presented and with water (450 ml) offset became. In a second vessel polyvinylpyrrolidone became (type K15) (10 g) and sodium CIT advice dihydrate (59 g) in water (500 ml) dissolved. The two solutions became subsequent mixed and bottom reflux up to the boiling point heated. One let the solution an hour simmer, a color change of red in very dark-brown occurred. After the solution was cooled, this Edelmetallkolloidsol (D could. h. this Pt-Nanopartikeldispersion) for the preparation of heterogeneous GET rising up ores catalysts used becomes.
2. 35.5 g of an aqueous solution of Natriumtetrachlorpalladat (Na_2PdCl_4) of 15 Gew. - % palladium content presented and with water (470 ml) mixed became. In a second vessel became polyvinyl alcohol (10 g), sodium CIT advice dihydrate (59 g) and ascorbic acid (35 g) in water (500 ml) dissolved. The two solutions became subsequent mixed and bottom reflux up to the boiling point heated. One let the solution an hour simmer, a color change of red in very dark-brown occurred. After the solution was cooled, this Edelmetallkolloidsol (D could. h. this Pd nano-particle dispersion) for the preparation of heterogeneous GET rising up ores catalysts used becomes.

Preparation of a supported catalyst

3. 198 g (dry matter) of a fine-particulate activated carbon dispersed became in water (800 ml) with the help of an ultrasonic bath. To this suspension a portion of the platinum oil represented in example 1 (125 ml) added and the mixture 5 minutes were mixed. The mixing suspension became by a filter membrane (z. B. from cellulose nitrate; Pore size 0.45 μm) filtered (the filtrate was complete decolorized, D. h. free of metal nano-particles).

The solid became extensively dried of the membrane on the membrane washed, separate and. This about 1 gew. - %ige Pt-catalyst could become direct the catalysis, for example the selective hydrogenation from nitrobenzene to aniline, used.



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1. Aqueous precious metal colloids in form of a sol with metal particles of a size from 0,5 to 100 Nm, obtained by reduction of precious metal connections by organic reducing agents and characterized through

- a) a precious metal content of more than 10 mmol per L sol,
 - b) content at water-soluble polymers from 0,1 to 20 Gew. - %,
 - c) content at organic solvents from 0 to 10 Gew. - %, everything related to the total weight of the sol, and
 - d) the remainder to 100 Gew. - % at waters,
- whereby additional oxidation products of the used reducing agents and excess reducing agents in the sol are present if necessary.

2. Method to the preparation of aqueous precious metal colloids with metal particles of a size from 0,5 to 100 Nm, characterised in that one to an aqueous solution of a precious metal salt or - complex or several water-soluble polymers adds and then the precious metal cation from them of a reduced, whereby with a metal content of more as 10 mmol/l to 500 mmol/l, several to the metallic state by addition of an organic reducing agent from the group of C1-C4-Alkoholen, C1-C4-Aldehyden, formic acid, ascorbic acid, citric acid, urea or other known organic reducing agents or a mixture, calculated than elemental metal, and an amount of the water-soluble polymer of 0, 1 to 20 Gew. - one works %, everything related to the total weight of the aqueous solution.

3. Method to the preparation of precious metal supported catalysts, characterised in that one a catalyst support with a precious metal colloid contained sol according to claim 1 in contact brings, the noble metal on the carrier to draw up leaves, so that the finished supported catalyst 0.1 to 20 Gew. - % noble metal, related to which total weight of the supported catalyst contains, which dries depleted sol remote and the supported catalyst at noble metal.

4. Precious metal colloids according to claim 1, characterized by additional content at polyvalent anions.

5. Precious metal colloids after claims 1 and 4, characterized by content at water-soluble polymers from the group of Poly N vinylpyrrolidon, polyacrylic acid, polymethacrylic acid, polyvinyl alcohol, Polyasparaginsäure or a mixture a several of them, preferred Poly N vinylpyrrolidon, with molecular weights (weight averages) of 15.000 to 1.500.000, preferred 30.000 to 1.000.000.

6. Precious metal colloids after claims 1, 4 and 5, characterized by a precious metal content of more as 10 mmol/l to 500 mmol/l, preferred more as 10 mmol/l to 250 mmol/l, particularly preferred more than 50 mmol/l to 250 mmol/l.

7. Precious metal colloids after claims 1 and 4 to 6, characterized by the addition of a not reducible Dotiermetalles from the group of Ti, Zn, Zr, Mo, Hf, Re, Ce, Lu, Ni, cu, preferred Ni, cu, in an amount from 0 to 100 Gew. - %, preferred 0 to 30 Gew. - %, related to the weight of the noble metal and calculated as metal.

8. Process according to claim 2, characterised in that the organic reducing agent in an amount from 100 to 5000%, preferred 150 to 2000%, particularly preferred 200 to 1000% of the stoichiometric need used becomes.

9. Process according to claim 2 and 8, characterised in that as organic reducing agents ascorbic acid, citric acid, methanol, ethanol or a mixture several of them, used becomes.